TOPIC 3:
States of Matter

Concept of state of matter
Solids
Gases
Liquids
Liquid crystals
Liquid-gas equilibrium
Solutions
Colligative properties

Concept of state of matter

- Concept of long and short range order
- According to the gradation in long range order:
  - Solids:
    - Crystalline
    - Amorphous and semicrystalline
    - Magnetically ordered
  - Liquids:
    - Liquid crystals
  - Gases:
    - Real gases
  - Plasma

Solids

- According to the bond nature:
  - Ionic and partially ionic solids (Ceramics)
  - Metals
  - Covalent solids (Diamond)
  - Molecular solids (Polymers)

Ionic solids

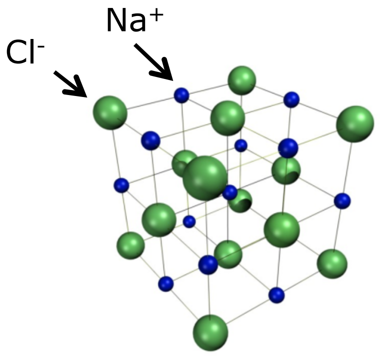
- Composed of ions
  - Electropositive atoms (metals) donate electrons to acceptors (electronegative atoms) forming ions. Ions are placed at fixed positions within a crystal. Highly crystalline.
  - Strong Coulombic interactions between ions
    - Energy to bring two ions from an infinite distance to an equilibrium distance

To avoid collapse of ionic structure

$$E_T = \frac{Z_1Z_2e^2}{4\pi\pi_0 r} + \frac{B}{r^n}$$

n: Born exponent (7.7 for NaCl)
B: arbitrary constant

- Energy to bring a mol of ions from an infinite distance to fixed position in a crystal: Lattice Energy.



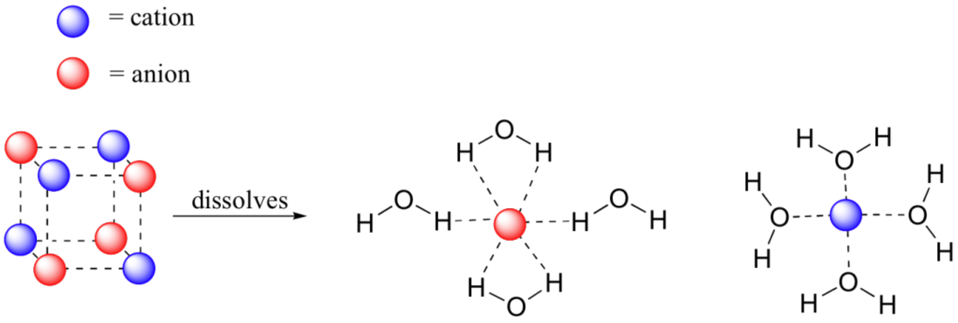
http://es.wikipedia.org/wiki/Archivo:Nacl-structure.jpg

$$U = -\frac{Z_1Z_2e^2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)\left(6-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\dots\right) = -\frac{Z_1Z_2e^2A}{4\pi\varepsilon_0 r_0}$$

A: convergent series of numbers related with the distances between ions of equal and opposite charge. Madelung constant

- Properties that depend on Lattice Energy:
  - High melting and boiling temperatures
  - High hardness
  - High modulus of elasticity (high charge and small radius)
  - Fragile (brittle) because of repulsions between ions of the same sign

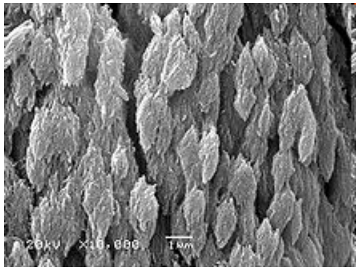
- Properties that depend on the nature of ionic bonding:
  - Do not conduct electricity (no free electrons)
  - Soluble in water and polar solvents: hydration or solvation: is an interaction of an ion (solute) with water (solvent), which leads to stabilization of the ions (solute species) in the solution. The energy of hydration is similar to the lattice energy: very exothermic.
    - The interaction is of the ion-dipole type. Cations are surrounded by the oxygen site of H_2O molecule and anions by the hydrogen site.
    - Each ion is surrounded by several shells of water molecules that extend radially



http://chemwiki.ucdavis.edu

- Bio-ceramics: hydroxyapatite
  - Main component of bones, dental enamel (dentin) and small calcifications
  - $Ca_{10}(PO_4)_6(OH)_2$: crystallizes in Hexagonal system. Mohs hardness: 5
  - Orthopedic implants made from these materials bond readily to bone and other tissues in the body without rejection or inflammatory reactions.
  - Most hydroxyapatite ceramics are very porous and lack mechanical strength and are used to coat metal orthopedic devices to aid in forming a bond to bone or as bone fillers.
  - They are also used as fillers for orthopedic plastic screws to aid in reducing the inflammation and increase absorption of these plastic materials.
  - Work is being done to make strong, fully dense nano crystalline hydroxyapatite ceramic materials for orthopedic weight bearing devices, replacing foreign metal and plastic orthopedic materials with a synthetic, but naturally occurring, bone mineral. Ultimately these ceramic materials may be used as bone replacements or with the incorporation of protein collagens, synthetic bones.

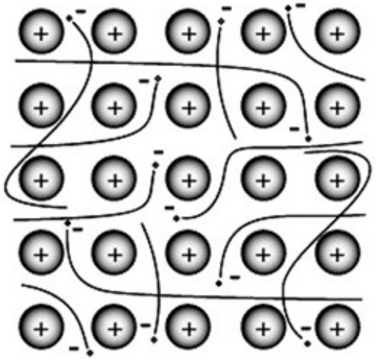
http://www.mylearning.org



Electronic magnification of bone mineral

http://en.wikipedia.org/wiki/
File:Bertazzo_S_SEM_deproteined_bone_-_cranium_rat_-

Metals



- *Metallic bonding*: electromagnetic interaction between delocalized electrons (conduction electrons) gathered in an "electron sea", and the metallic nuclei within metals: sharing of "free" electrons among a lattice of positively charged ions (cations).

http://www.ibegham.com/wiki/tiki-index.php?page=Introducing+and+Classifying+Materials

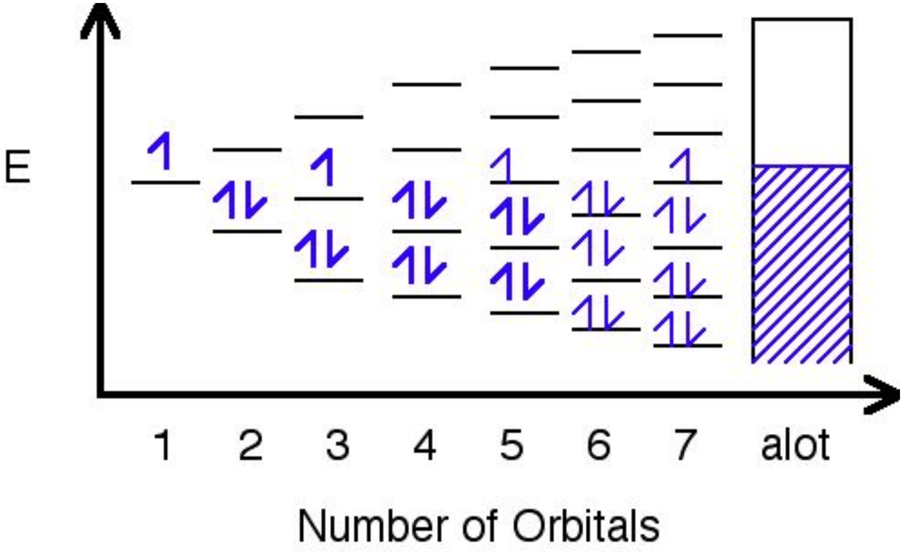
• Bonding energy depends on the number of shared electrons and on the radius of cations

If nº e ↑and r ↓ then T_M ↑: Wolfram (Tungsten): 3422 ºC
If nº e ↓ and ↑ r then T_M ↓ : Rubidium: ~40 ºC

A remarkable exception are the elements of the zinc group: Zn, Cd, and Hg. Their electron configuration ends in ...ns^2 resembling a noble gas configuration and the energy distance to the empty np orbitals becomes larger as we go down in the periodic table.

•As a consequence, there is range in mechanical properties (ductility, modulus of elasticity) from soft metals (sodium) to strong metals (Wolfram, E = 400 GPa)
•An interesting linguistic discussion on Wolfram or Tungsten. IUPAC accepts Tungsten but Spanish members doesn't

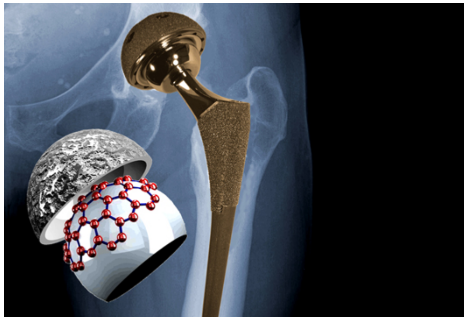
- Band theory: a metallic bond is formed when all the atomic orbitals are combined in a single molecular orbital



http://chemwiki.ucdavis.edu/Theoretical_Chemistry/Chemical_Bonding/Metalic_Bonding

- An energy band is formed with very small energy difference between levels: a small electric field can promote electrons to unoccupied higher energy levels appearing electronic conduction.
- Alternative view: Electrons within a metal are inside a potential well. The maximum energy of the electrons at 0 K is called Fermi Level. The energy required to detach an electron from the metal is called Work Function

- Titanium: Sometimes called the "space age metal", it has a low density and is a strong, lustrous, corrosion-resistant (including sea water, aqua regia and chlorine) transition metal with a silver color.
- Its modulus of elasticity nearly matches that of the bones thus allowing an even distribution of skeletal loads.
- Orthopedic implants
  - Biocompatible (non-toxic and is not rejected by the body): titanium is used in a gamut of medical applications including surgical implements and implants, such as hip balls and sockets (joint replacement) that can stay in place for up to 20 years. The titanium is often alloyed with about 4% - 6% Al and 4% vanadium.



http://www.futurity.org/health-medicine/how-to-build-a-better-hip-graphite/

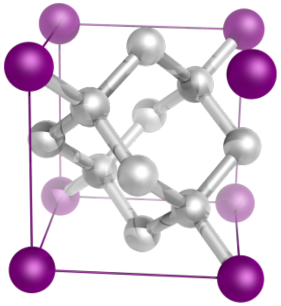
  - Osseointegrating metal: enabling use for over 30 years.
  - Since titanium is non-ferromagnetic, patients with titanium implants can be safely examined with magnetic resonance imaging

Covalent solids

- Covalent solid or covalent network: atoms are bonded by covalent bonds in a continuous network. There are no individual molecules and the entire crystal may be considered a macromolecule.

- Because of high bonding energy and electron localization, covalent solids are very strong and do not conduct electricity

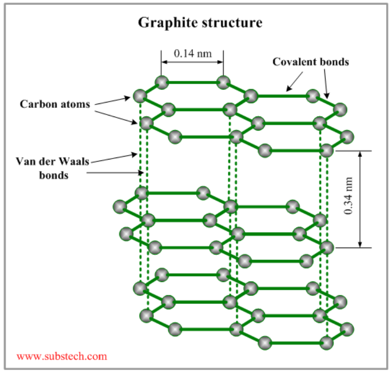
- Examples
  - Diamond with a continuous network of carbon atoms



http://en.wikipedia.org/wiki/File:Carbon_lattice_diamond.png

  - Silicon dioxide or quartz with a continuous three dimensional network of SiO_2 units.

  - Graphite and the mica group of silicate minerals structurally consist of continuous two dimensional layers covalently bonded within the layer with other bond types holding the layers together.



http://www.substech.com/dokuwiki/doku.php?id=graphite

Molecular solids

- Solids composed of molecules held together by the van der Waals forces.
- Because these dipole forces are weaker than covalent or ionic bonds: soft and low melting temperature. Because electron localization: electrical insulators.
- Examples: hydrocarbons, ice, sugar, fullerenes,….Small molecules
  - Long molecules: polymers. Amorphous or semi-crystalline
  - Polymers with biological relevance:

- Polysaccharides, proteins, nucleic acids
- Biodegradable polymers: natural polyesters produced by a wide variety of bacteria as intracellular reserve materials or by polymerization of bacterial produced monomers
  - Possible applications as biodegradable, melt processable polymers from renewable resources.
  - Properties vary from rigid brittle plastics, to flexible plastics with good impact properties to strong tough elastomers, depending on the particular structure.

- Poly-β-hydroxybutyrate (PHB), and poly(lactic acid ester) (PLA): representative.
  - Highly crystalline with a melting temperature around 180°C and a glass transition temperature (softening temperature) ranging from 5°C (PHB) to 65 ºC (PLA). These properties make them very brittle.
  - The main degradation mechanism is hydrolysis and chain scission. A progressive increase in porosity facilitates the diffusion by removal of degradation products

Solids: Summary *(complete the chart)*

Kind of solid	Particles on lattice	Inter-molecular forces	Properties	Examples
Ionic				
Metallic				
Covalent				
Molecular (Short molecules)				
Molecular (Long molecules)				

Gases

- Fundamentals
  - Pressure p = f/A; SI units: 1 Pa = 1 $kg\cdot m^{-1}\cdot s^{-2}$; other units: 1 atm = $1.01325\cdot 10^5$ Pa = 760 torr; 1 torr = 133.322 Pa; 1 bar = 10^5 Pa
  - Boyle's law, $p\cdot V$ = constant
  - Charles and Gay-Lussac's law, p/T = constant; V/T = constant
  - Avogadro's principle: at fixed P and T, no molecules of gas ocuppy the same volume regardless of its chemical identity
  - All above can be groups into the "ideal gas law" $P\cdot V = n\cdot R\cdot T$; R = <gas constant> = 0.08206 $atm\cdot L\cdot mol^{-1}\cdot K^{-1}$ = 8.31447 $J\cdot K^{-1}\cdot mol^{-1}$=1.986 $cal\cdot mol^{-1}\cdot K^{-1}$
  - Molar concentration of a gas n/V = p/RT
  - Density [illegible] = Mp/RT
  - Dalton's law of mixture of gases $p_T = \Sigma p_i$; p_i = <partial pressure>
  - Mixture of gases $p_i = \mathbf{y}_i\cdot p_T$; $\mathbf{y}_i$ = <molar fraction of **gas** *i*>

A kinetic theory of gases

Four statements:

A gas is essentially empty space.

Molecules (dots) are constantly moving in a chaotic way: average velocity. $\overline{u}$

Collisions are elastic: no intermolecular interactions and moment is preserved.

Each part the average energy is composed of, is proportional to absolute temperature.

$$\overline{E}_{part} = \frac{1}{2}kT$$

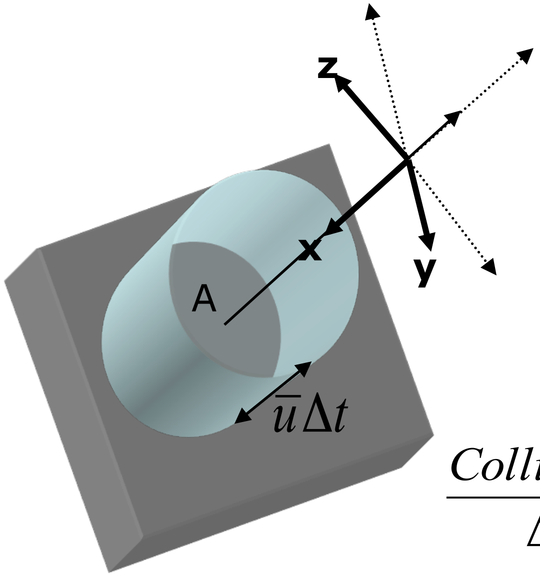
Since there are no intermolecular interactions, potential energy is zero and molecules (dots) only posses kinetic energy due to translation

$$\overline{E} = \overline{E}_C = \frac{1}{2}m\overline{u}^2 = \frac{1}{2}m(\overline{u}_x^2 + \overline{u}_y^2 + \overline{u}_z^2) = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT$$

This is a consequence of the Equipartition of energy theorem from Statistical Mechanics: *in thermal equilibrium, energy is shared equally among all of its various forms.*

Pressure is a consequence of collisions with the walls of the container. Since collisions are elastic, momentum and energy are preserved.

Assume a container of volume V that contains N molecules with average velocity $\bar{u}$
Let us draw a virtual cylinder emerging from the wall of A cross-section and length $\bar{u}\Delta t$
This cylinder contains all molecules that will collide with the wall within a time *Δt*
Collisions with the wall originate the pressure. We will calculate it:



$$p = \frac{f}{A} \qquad f = \frac{\Delta p\ in\ wall}{\Delta t} = \frac{\Delta p\ in\ wall}{Collision} \times \frac{Collisions}{\Delta t}$$

$$\frac{\Delta p\ in\ molecule}{Collision} = \Delta(m\bar{u}) = -m\bar{u} - m\bar{u} = -2m\bar{u}$$

$$\frac{\Delta p\ in\ wall}{Collision} = +2m\bar{u}$$

$$\frac{Collisions}{\Delta t} = \frac{n^o\ molec.\ in\ cylinder\ moving\ \text{-}\ x}{\Delta t} = \frac{1}{6} \times \frac{N}{V} \times A\bar{u}\Delta t \times \frac{1}{\Delta t}$$

Nuestra

$$p = \frac{f}{A} = \frac{1}{A} \times 2m\bar{u} \times \frac{1}{6} \times A\bar{u}\Delta t \times \frac{N}{V} \times \frac{1}{\Delta t} = \frac{1}{3}\frac{Nm\bar{u}^2}{V}$$

$$pV = \frac{1}{3}Nm\bar{u}^2 = \frac{2}{3} \times N \times \frac{m\bar{u}^2}{2} = \frac{2}{3} \times N \times \frac{3}{2}kT = nN_AkT = nRT$$

Mahan (1990) p.46
Atkins (2010) p. 153
http://en.wikipedia.org/wiki/Kinetic_theory

Equation of state of an ideal gas

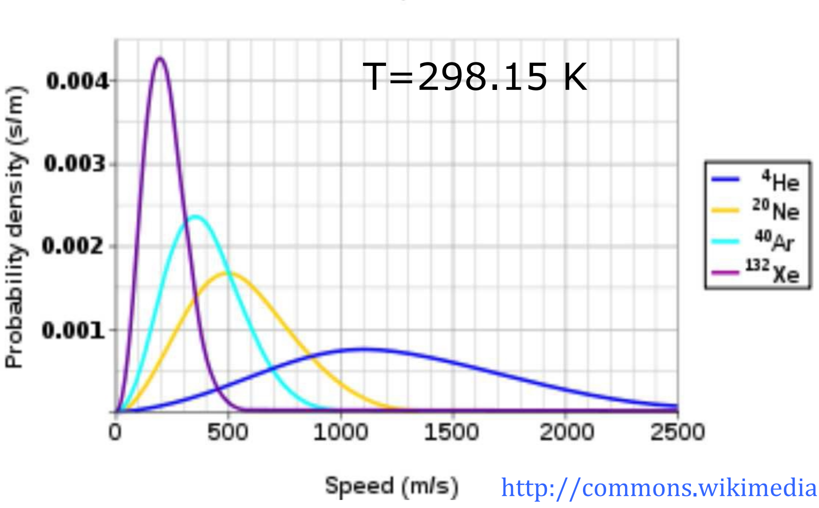
What is an "equation of state"? *A thermodynamic relation between* *__state variables__* *that defines the state of matter*

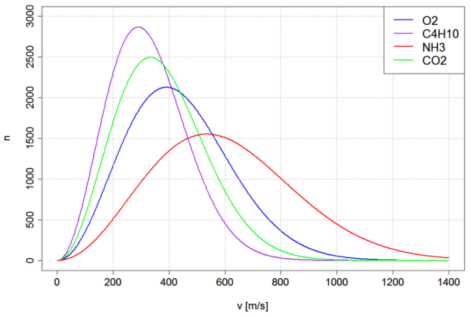
$$p = \frac{RT}{V} \Rightarrow \boxed{pV = nRT}$$

For 1 mole — For n moles

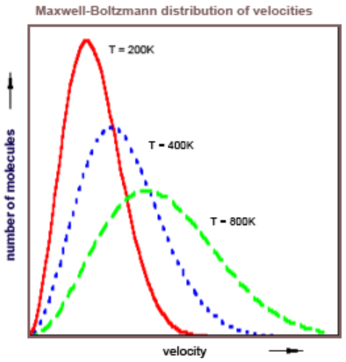
Average speed

$$\boxed{\begin{aligned} &pV = \frac{1}{3} N \cdot m \cdot \overline{u}^2 = \frac{1}{3} n \cdot N_A \cdot m \cdot \overline{u}^2 = \frac{1}{3} n \cdot M \cdot \overline{u}^2 = nRT \\ &\overline{u} = \sqrt{\frac{3RT}{M}} \end{aligned}}$$





http://commons.wikimedia.org/wiki/File:Maxwell-Boltzmann_speed_distributions.png



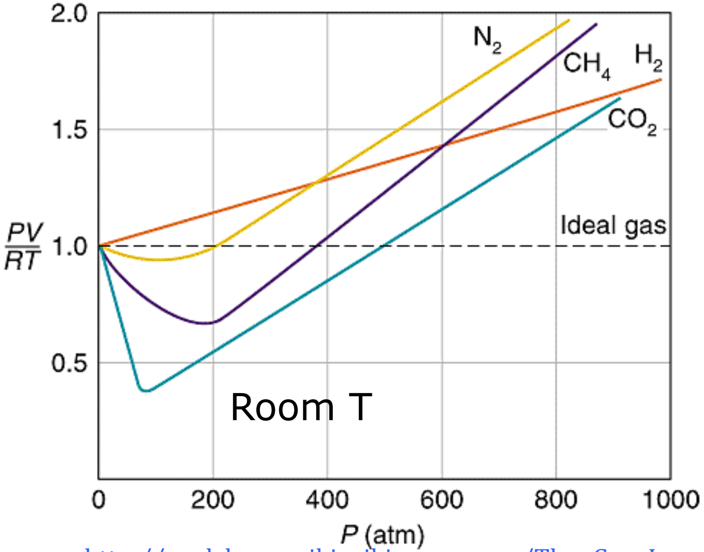
http://www.informationphilosopher.com/introduction/physics/

http://commons.wikimedia.org/wiki/File:MaxwellBoltzmann.gif?uselang=fr

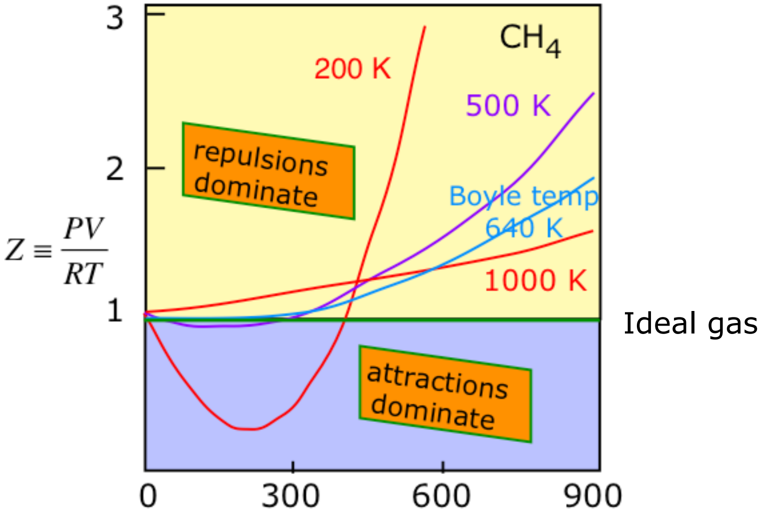
Real gases

- Ideal gas equation predicts that the compressibility factor should be independent on temperature and pressure. For n = 1

$$z = \frac{pV}{RT} = 1$$



http://mrdchemawiki.wikispaces.com/The+Gas+Laws



http://www.summitcds.org/chem1vt/webtext/gas/gas_6.html

- At low pressures, the behavior is dominated by attractive forces making z <1

- At high pressures, because molecules occupy volume instead of being mass points, repulsive forces appear; the volume of the real gas (V_{real}) becomes greater than the volume of an ideal gas (V_{ideal}) which causes z >1

- At low pressures and high temperatures, deviations from ideal behavior are small

The most common equations to describe real gas behavior are: Van der Waals and the Virial equation.

$$\frac{PV}{RT} = nRT\cdot(1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m{}^2} + \frac{D(T)}{V_m{}^3} + \ldots$$

B(T), C(T) are called second virial coefficient, third virial coefficient and so on; V_m is the molar volume

$$(P + a\frac{n^2}{V^2})(V - nb) = nRT \qquad b = 4V_m N_A; \qquad a = bRT_{Boyle}$$

Parameter _a_ represents the role of attractions between molecules slowing down collisions with the wall. It is a correction for pressure.

Parameter _b_ represents the role of repulsions due to the volume occupied by molecules that excludes others. It is correction for volume

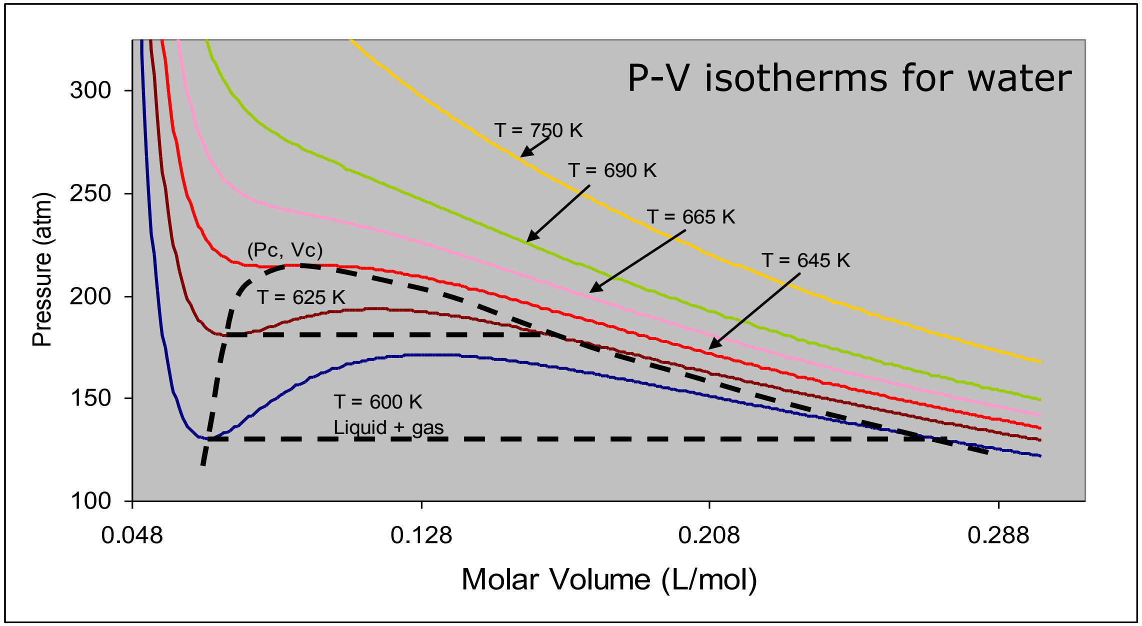
Van der Waals parameters

Gas	a (L^2 atm mol^{-2})	b (L mol^{-1})
Ammonia	4.225	3.707
Argon	1.363	3.219
Benzene	18.24	11.54
Carbon dioxide	3.640	4.267
hydrogen	0.2476	2.661
water	5.536	3.049

These parameters are obtained experimentally.

Real gases: Liquefaction

- At high temperatures, average kinetic energy is higher than intermolecular attractive potential.
- As temperature is decreased the kinetic energy of some molecules begins to be less than the intermolecular potential and dimers or molecular associations form.
- At sufficiently enough low temperatures these associations extend to more molecules and a liquid forms.



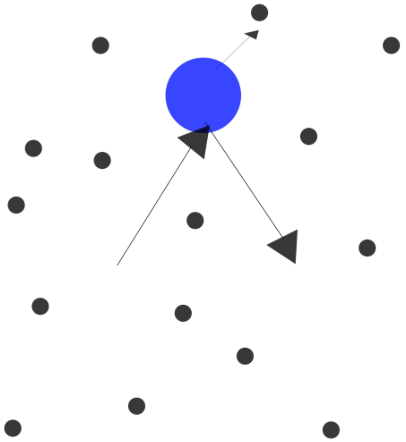
•This behavior is predicted by the Van de Waals equation.
•There is a temperature above which it is impossible to liquefy a gas. A dense supercritical fluid is obtained instead.
<u>Critical temperature: Tc</u>
•Below Tc, a gas transforms into a liquid by effect of pressure.
Intersections between the minimum on the left and the isotherms define the <u>Gas-Liquid Coexistence Region.</u> Inside this region, isotherms are nonsensical.

•The intersection of the critical isotherm with the gas-liquid coexistence region is the critical point, with critical coordinates (Pc, Vc).
•At the critical point an inflection is observed. It can be calculated applying elementary calculus on the Van der Waals equation.

Liquids

- Brownian motion: http://www.youtube.com/watch?v=iB7Eu7U73qg&feature=related

- As in gases, molecules in liquids have a characteristic chaotic movement with an average kinetic energy that depends on temperature. There is also a distribution of molecular velocities.
- Average intermolecular distances are shorter than in gases: intermolecular interactions are stronger.
- In liquids there is short range order not long range order



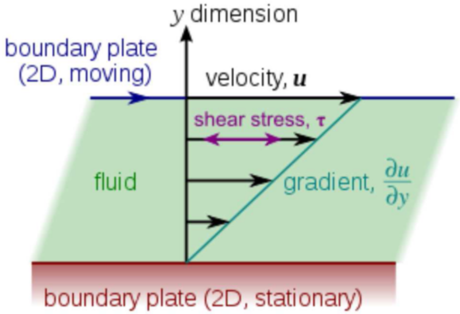
http://commons.wikimedia.org/wiki/File:Brownian_motion_2.svg

- **Viscosity**: is a measure of the resistance of a fluid to flow. Consequence of intermolecular forces and on the molecular structure (entanglements).

Units: Pascal-second (Pa·s), (equivalent to N·s/m^2, or kg/m·s). If a fluid with a viscosity of one Pa·s is placed between two plates of area A, and one plate is pushed sideways with a shear stress of one pascal, it moves a distance equal to the thickness of the layer between the plates in one second.

Derived unit: Poise. 1 Pa·s = 1 kg·m^{-1}·s^{-1} = 10 P

Liquids	Viscosity (mPa·s) at 25 ºC
Water	0.894
Mercury	1.526
Olive oil	81
Blood	3-4 (37 ºC)
Ethanol	1.074
Glycerol	1490



http://en.wikipedia.org/wiki/File:Laminar_shear.svg

$$\frac{F}{A} = \tau = \mu \frac{du}{dy}$$

A question to think about: *why olive oil is much more viscous than water if intermolecular forces in water are stronger than in olive oil*

- **Surface tension**: Surface tension is a property of the liquid's interface with another medium and measures the resistance of the surface to be deformed by an external force.

The cohesive forces among the liquid molecules are responsible for this phenomenon of surface tension. In the bulk of the liquid, each molecule is pulled equally in every direction by neighboring liquid molecules, resulting in a net force of zero. The molecules at the surface do not have other molecules on all sides of them and therefore are pulled inwards. This creates some internal pressure and forces liquid surfaces to contract to the minimal area.

Surface tension (γ): is work done on the surface of a liquid to increase its surface the unit area.

If the surface of a mass of liquid is A and we want to increase it by *δA* , the work we need is γ*δA*. This work is stored as potential energy.
Units: (SI) joules per square meter

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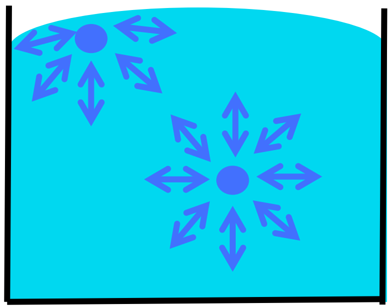


Effects:
- Contact angle between a liquid and a solid
- Capillarity

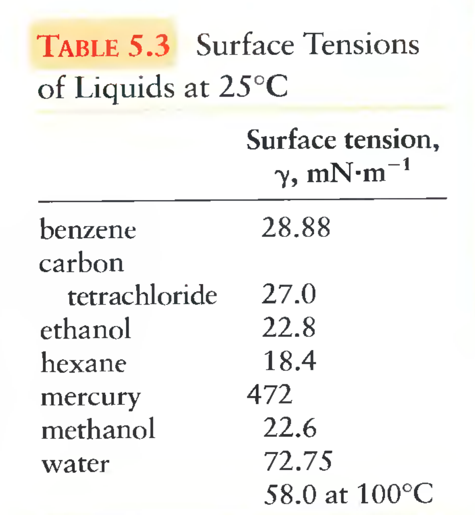
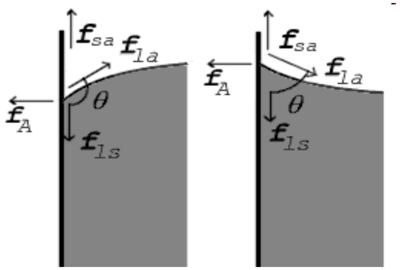


TABLE 5.3 Surface Tensions of Liquids at 25°C

	Surface tension, γ, $mN \cdot m^{-1}$
benzene	28.88
carbon tetrachloride	27.0
ethanol	22.8
hexane	18.4
mercury	472
methanol	22.6
water	72.75 58.0 at 100°C

Effects of surface tension:

- Contact angle between a liquid and a solid
Results from the balance between different forces:
Liquid-solid, solid-air, liquid-air

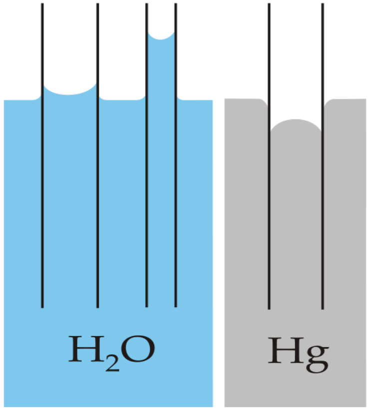


http://en.wikipedia.org/wiki/Surface_tension

$\theta > 90$
Hg/soda glass ~ 140º

$\theta < 90$
H_2O/soda glass ~ 0º

- Capillarity



http://en.wikipedia.org/wiki/File:Capillarity.svg

$$h = \frac{2\gamma\cos\theta}{\rho g r}$$

- Flotation. Objects denser than water float when the object is nonwettable and its weight is small enough to be borne by the forces arising from surface tension. Water Striders

http://en.wikipedia.org/wiki/Surface_tension

Liquid crystals

Are a state of matter that, in a given set of temperature and composition conditions, have properties between those of a conventional liquid and those of a solid crystal, they may flow like a liquid, but its molecules may be oriented in a crystal-like way.

Classification

Depending on which variables induce the liquid crystal behavior they can be classified in:

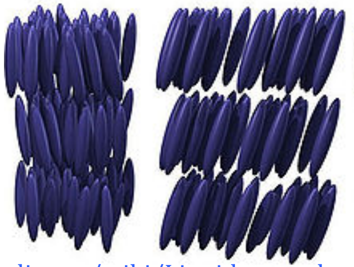
- Thermotropic (organic): temperature induces a phase transition into the LC phase
- Lyotropic (organic): phase transitions as a function of both T and concentration of the LC in a solvent (water).
- Metallotropic (inorganic-organic): LC transition depends on T, conc. and on the inorganic-organic composition.

Structures

- Thermotropic

Nematic

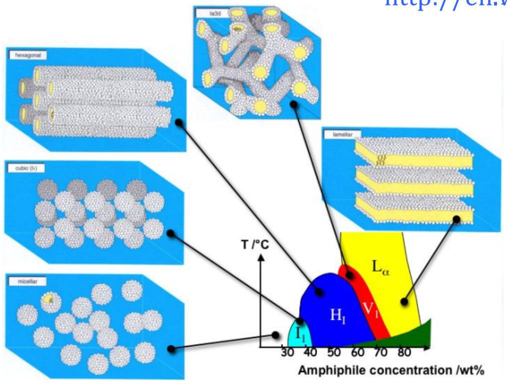
Smectic



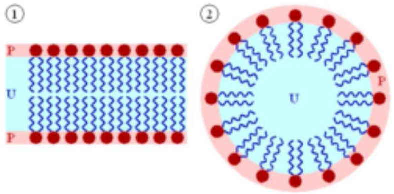
Chiral

http://en.wikipedia.org/wiki/Liquid_crystal

- Lyotropic



http://en.wikipedia.org/wiki/Lyotropic_liquid_crystal

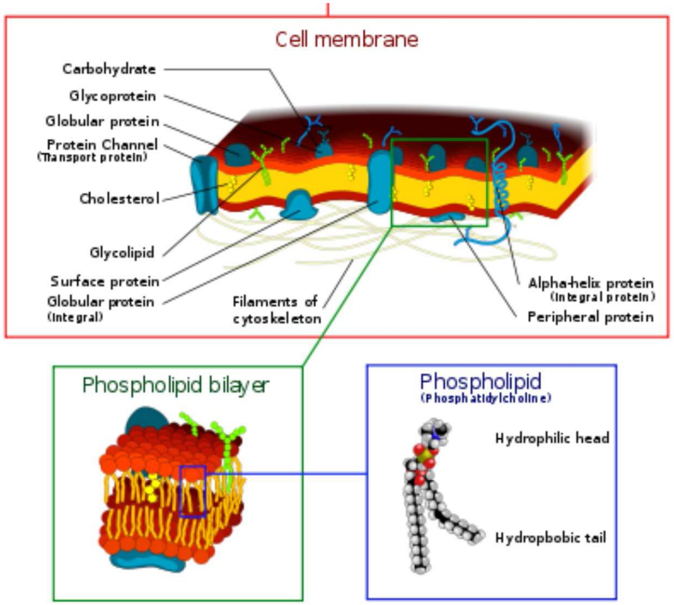


Micelles in water-soap solutions

http://en.wikipedia.org/wiki/Liquid_crystal

Biological membranes and cell membranes are a form of LC.

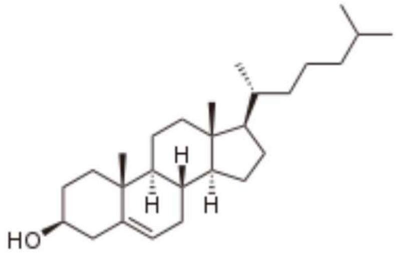
Their constituent molecules (e.g., phospholipids) are perpendicular to the membrane surface, yet the membrane is flexible. The constituent molecules can inter-mingle easily, but tend not to leave the membrane due to the high energy requirement of this process.



http://en.wikipedia.org/wiki/Cell_membrane

Spider silk is a form of LC.
The concentrated protein solution that is extruded by a spider to generate silk is a liquid crystal phase. The precise ordering of molecules in silk is critical to its renowned strength.

Cholesteric LC
Some cholesterol derivatives, (among other simple cholesteric lipids) are known to generate the liquid crystalline cholesteric phase. The cholesteric phase is in fact a chiral nematic phase, and changes colour when its temperature changes. This makes cholesterol derivatives useful for indicating temperature in liquid crystal display thermometers and in temperature-sensitive paints



Liquid-gas equilibrium

Since there is a distribution of velocities, those surface molecules with energy higher than necessary to overcome intermolecular attractions (hot molecules) will pass to the vapor state.

If the system is open: all liquid will pass to vapor state: evaporation

If the system is closed: evaporation proceeds until the "cold gas molecules" collide on the liquid surface becoming trapped by the liquid (condensation).

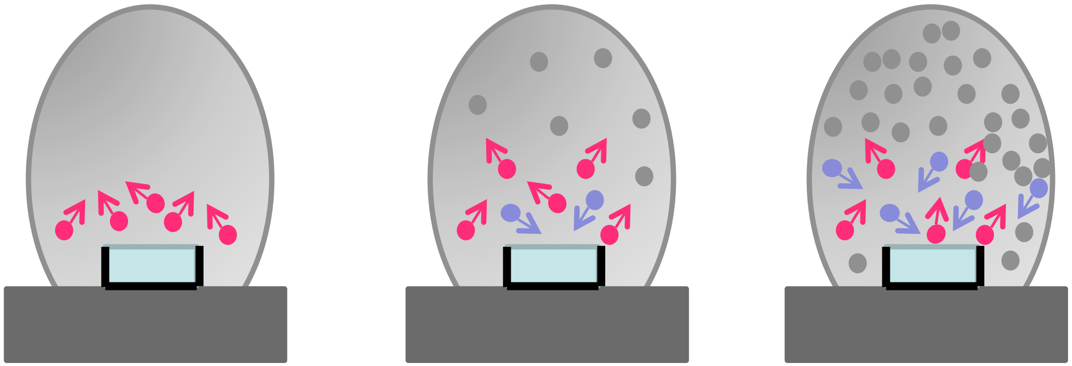
Liquid-vapor equilibrium : condensation rate = evaporation rate

As liquid evaporates the vapor exerts a pressure on the walls of the container. At equilibrium and at constant temperature, this pressure is called **Vapor Pressure**

● Molecules in vapor state

●→ Molecules undergoing vaporization

●→ Molecules undergoing condensation



Nuestra

Dependence of Vapor pressure on Temperature

As temperature is raised, kinetic energy of liquid molecules increases being easier to evaporate. Vapor pressure increases therefore.

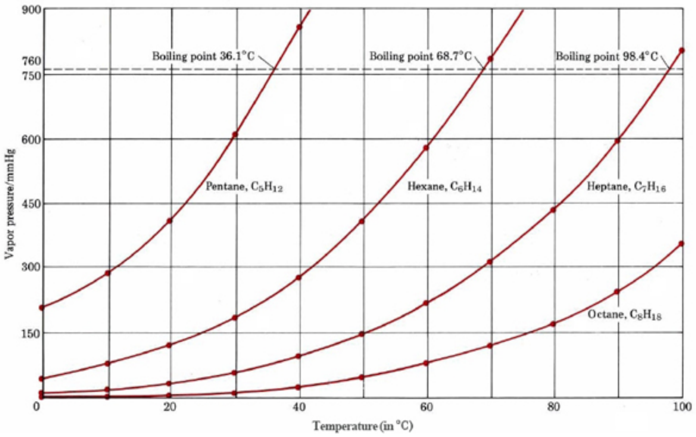
Normal Boiling Temperature: temperature at which vapor pressure is 1 atm

Clausius equation

On a pressure–temperature (P–T) diagram, the line separating the two phases is known as the coexistence curve. The Clausius–Clapeyron relation gives the slope of this curve. Mathematically

$$\boxed{\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}}$$

ΔH: change in enthalpy for the change of state (latent heat)
ΔV: change of volume for the change of state



http://chemguide.wikispaces.com/U9.3+Vapor+pressure+and+phase+diagrams

Clausius-Clapeyron equation. Particular case of the Clausius equation for vaporization and sublimation processes.

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V_{L-V}} = \frac{\Delta H_V}{T(V_V - V_L)} \approx \frac{\Delta H_V}{TV_{gas}} = \frac{p\Delta H_V}{RT^2} \Rightarrow \frac{dp}{p} = \frac{\Delta H_V}{RT^2}dT$$

$$\boxed{V = \frac{RT}{p}}$$

$$\int_1^2 \frac{dp}{p} = \int_1^2 \frac{\Delta H_V}{RT^2}dT = Ln(p_2) - Ln(p_1) = \frac{\Delta H_V}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

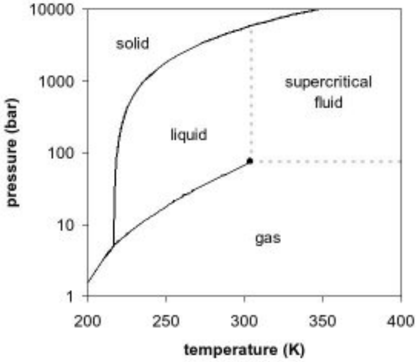
$$\boxed{Ln\left(\frac{p_2}{p_1}\right) = \frac{\Delta H_V}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

Equilibrium Phase Diagrams.

Chart used to show conditions at which thermodynamically distinct phases can occur at equilibrium.

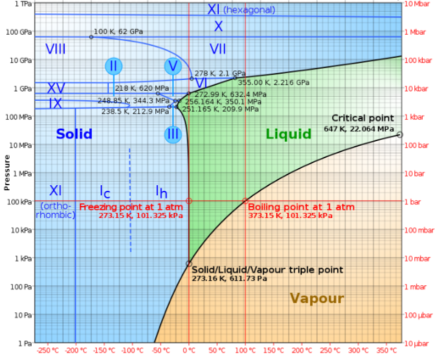
Phase rule: f (degrees of freedom) = c (component) – p (phases) + 2

CO_2



http://en.wikipedia.org/wiki/File:Carbon_dioxide_pressure-temperature_phase_diagram.jpg

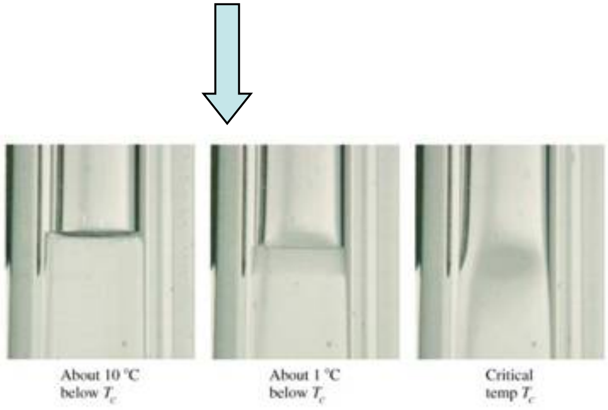
H_2O



https://256.makerslocal.org/wiki/File:Phase_diagram_of_water.svg

Triple point: three phases coexist (O).

Critical point (C).


About 10 °C below T_c

About 1 °C below T_c

Critical temp T_c

A question to think about: *why the S-L slope for CO_2 is positive while it is negative for water?*

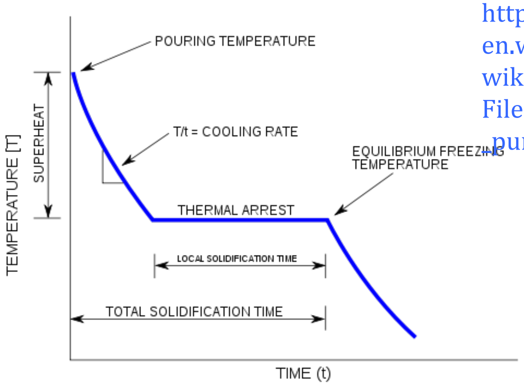
How Equilibrium Phase Diagrams are obtained?

At constant pressure, temperature remains constant until the transformation is complete

The system is heated at constant pressure and temperature is recorded as a function of time.

In the time ranges AB and CD heat is used to change the state of the system: to overcome intermolecular attractions.

In the time ranges Initial-A, BC and D-Final, heat is used to increase temperature.



http://en.wikipedia.org/wiki/File:Cooling_curve_pure_metal.svg

Solutions

Homogeneous mixture composed of two or more substances. In such a mixture, a solute is dissolved in another substance, known as a solvent. Solutes can be:

Electrolytes: dissociate in ions
Non-electrolytes: no dissociation

Solubility

Saturated solution: a solution is said saturated when the solvent has dissolved all the solute it can and some solute remains undissoved
Molar solubility: the molar concentration of a saturated solution
Gold rule: like-dissolves-like

When a solute dissolves in a liquid solvent, solute-solute attractions must be replaced by NEW solute-solvent attractions. If these are similar to those replaced, very little energy is required for the solution to form. If the main attractions in the solute are hydrogen bonding (glucose), we must select a hydrogen bonding solvent like water. If the main attractions are London forces (sulfur) we must use a similar solvent CS_2

Solubility of gases

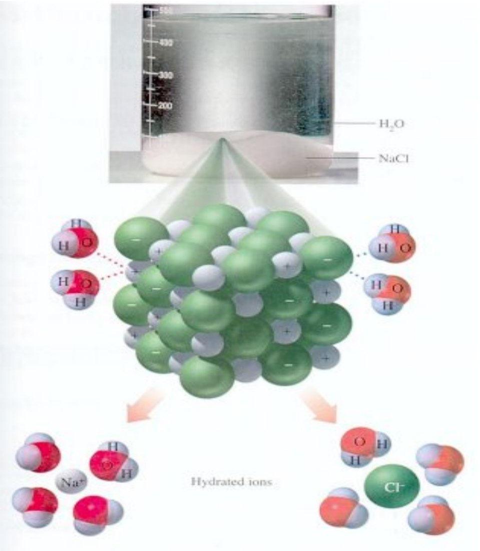
Henry's law: solubility of a gas is directly proportional to its partial pressure $s_i = k_H \cdot p_i$

Solubility of gases decrease with temperature

Gas (in water @ 20ºC)	k_H (mol L^{1} atm^{-1})
O_2	$1{,}3 \times 10^{-3}$
N_2	$7{,}0 \times 10^{-4}$
CO_2	$2{,}3 \times 10^{-2}$
He	$3{,}7 \times 10^{-4}$

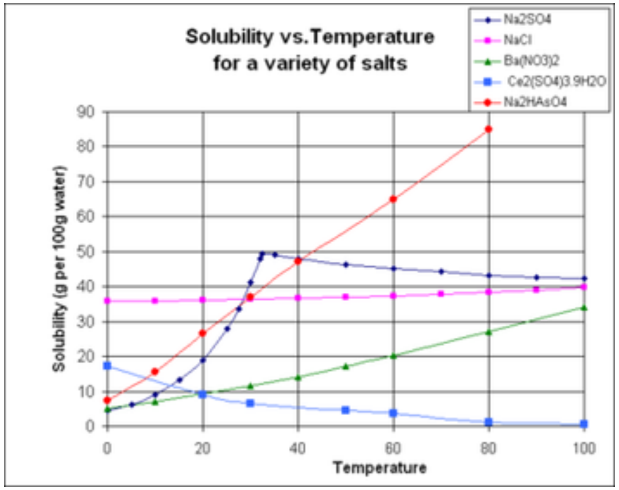
Solubility and temperature

In contrast to gases, most ionic and molecular solids are more soluble at high temperatures although they show a more varied behavior (for example Na_2SO_4). Variations can be explained in terms of enthalpy and entropy of solution



https://www.e-education.psu.edu/earth540/content/c3_p4.html

Anion-water an cation water interactions are exothermic: the released heat is called hydration enthalpy



http://chemicalscompelex.wikispaces.com/How+does+the+temperature+affect+the+solubility+of+a+substance

Solution process can be understood as a two step process:

1) The lattice is broken and ions go to gas phase (lattice enthalpy, ΔH_L, is consumed)
2) Ions in gas phase interact with water (hydration enthalpy, ΔH_{HYD}, is released)

Balance $\Delta H_{SOLUTION} = - \Delta H_L + \Delta H_{HYD}$.

For NaCl, this balance is +3 kJ/mol endothermic. Why is it spontaneous?

Colligative properties

Properties that depend on the number of solutes rather than in their chemical identity are called colligative properties:

- **Vapor pressure depression**
- **Boiling point elevation**
- **Freezing point depression**
- **Osmosis**

Vapor pressure depression.

Raoult's law: The vapor pressure of a solvent is proportional to its molar fraction in a solution. As a consequence, vapor pressure decreases as non volatile solutes are dissolved.

$$p_i = x_i p_i^0$$

p_i = partial vapor pressure of component i in the solution

x_i = molar fraction of component i in the solution

p_i^0 = vapor pressure of pure component i

For a binary AB solution, where A is solvent and B is a nonvolatile solute

$$p_T = p_A + p_B = x_A \cdot p_A^0 + x_B \cdot 0 = (1 - x_B) \cdot p_A^0$$

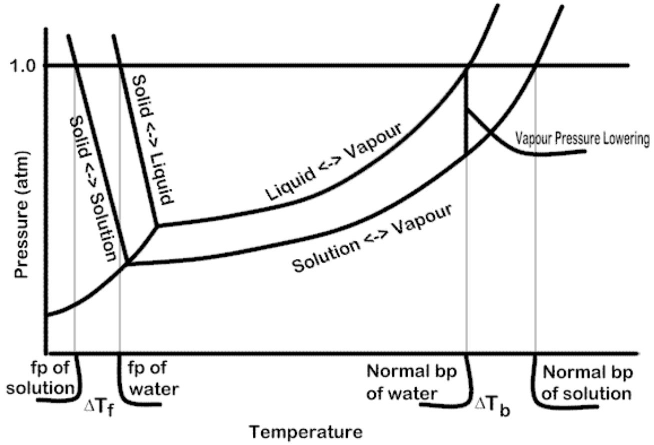
Boiling Point Elevation (Ebullioscopy)

If vapor pressure of solvent decreases if a solute is dissolved, then, at the boiling point, vapor pressure will not reach 1 atm value and it will be necessary to heat to higher temperatures to boil the solution. The boiling point elevation is proportional to the molality *m*.

$$\Delta T_b = T_b - T_b^0 = K_b m$$

Freezing point depression (Cryoscopy)

The effect of adding a solute to a solution consists of an expansion of the P, T range in which the solution exists in the liquid state. Boiling point increases and freezing point decreases. The freezing point depression is also proportional to the molality *m*.



http://www.hcchrisp.blogspot.com.es

$$\Delta T_c = T_c^0 - T_c = K_c m$$

T_b, T_c = Normal boiling point and freezing point of the solution

T_b^0, T_c^0 = Solvent normal boiling point and freezing point

K_b = Ebullioscopic constant

K_c = Crysocopic Constant

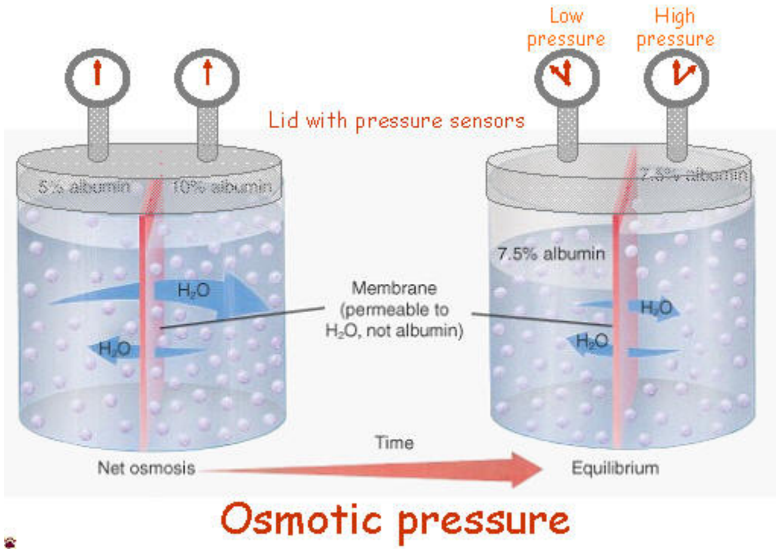
Osmotic Pressure

Osmosis: is the movement of water molecules across a partially-permeable membrane from a diluted solution through a concentrated solution.

Partially-permeable membrane: allows passage of solvent molecules but not solute molecules.

Osmotic Pressure (π): Is the needed pressure to stop osmosis. It is proportional to T and molar concentration

$$\pi = MRT$$



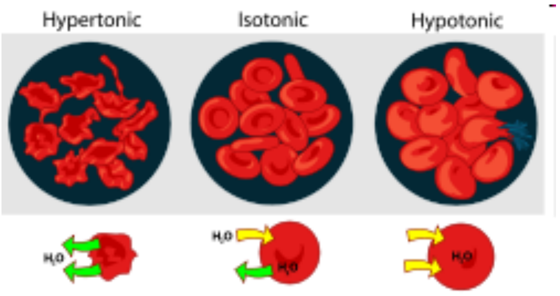
http://www.lionden.com/slides-cell.htm

Passive transport in cells

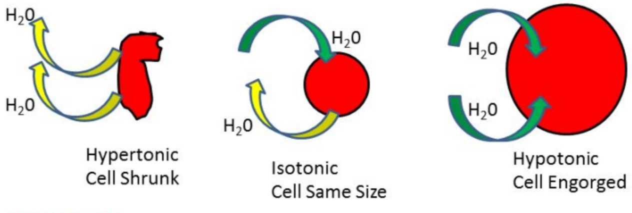
Moving biochemicals and atomic or molecular substances across the cell membrane without involveing chemical reactions. The four main kinds of passive transport are diffusion, facilitated diffusion, filtration and **osmosis**.

Transport of water across the cell membrane depends on the relative concentration of water on the outer and inner regions of a cell:

1. Hypertonic medium - a concentrated solution: the cell will lose water by osmosis.
2. Isotonic medium - a solution with exactly the same water concentration as the cell: no net movement of water across the cell membrane.
3. Hypotonic medium - a dilute solution: the cell will gain water through osmosis.



https://commons.wikimedia.org/wiki/File:Osmotic_pressure_on_blood_cells_diagram-es.svg



tristupe.com

http://www.tristupe.com/2012/02/overhydration-leading-to-hypoatremia.html

Colligative properties of electrolyte solutions

Colligative properties are the same as in non-electrolytes but multiplied by the Van't Hoff factor: number of ions produced by dissociation of the ionic compound.

Factor de Van't Hoff:

$$i = \frac{n^o\ particles\ after\ dissociation}{n^o\ particles\ before\ dissociation}$$

Boiling point elevation (Ebullioscopy)	$\Delta T_b = iK_b m$
Freezing point depression (Cryoscopy)	$\Delta T_c = iK_c m$
Osmotic pressure	$\pi = iMRT$

Think about: how to obtain the molar mass of a substance from colligative properties?

Binary solutions: volatile components

Vapor pressure

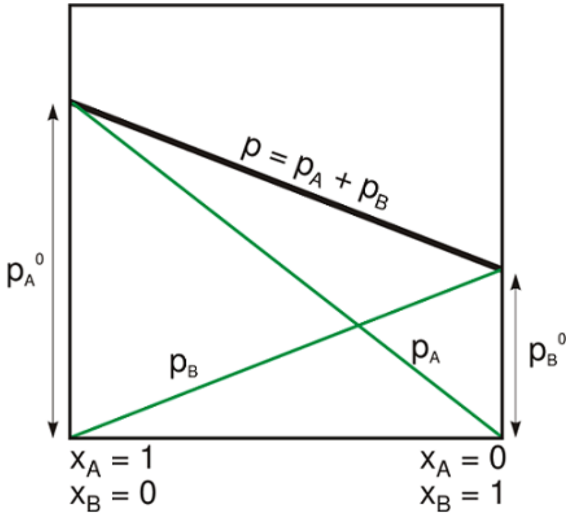
IDEAL MIXTURES OF LIQUIDS FOLLOW Raoult's law. Solution vapor pressure can be calculated as a function of composition of the liquid

$$p_i = x_i p_i^0$$

$$p_T = p_A + p_B = x_A \cdot p_A^0 + x_B \cdot p_B^0 =$$

$$= (1 - x_B) \cdot p_A^0 + x_B \cdot p_B^0 == p_A^0 + x_B (p_B^0 - p_A^0)$$

$$p_i = y_i p_T$$



http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Gases/Vapor_Pressure

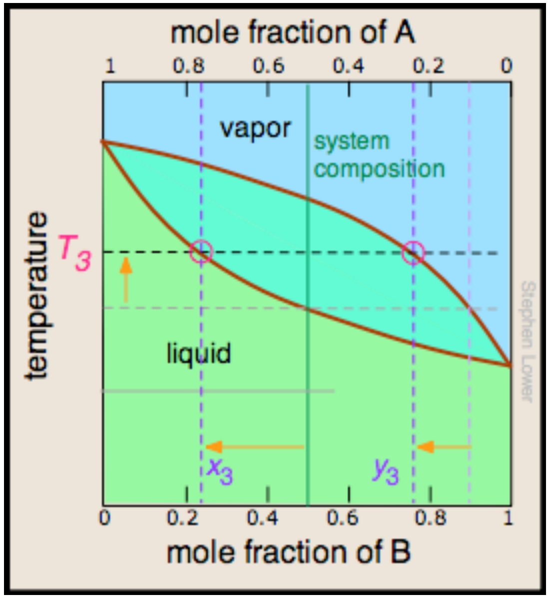
What is the composition of the vapor? We need Dalton's law
For a binary mixture AB

$$y_A = \frac{p_A}{p_T} = \frac{p_A}{p_A + p_B} = \frac{x_A p_A^0}{x_A p_A^0 + (1 - x_A) p_B^0}$$

If $p^0_A > p^0_B$ then $y_A > y_{B,}$
The vapor of an ideal mixture of two volatile liquids is richer in the more volatile component.

Volatile component: higher vapor pressure at a given temperature or lower boiling point at a given pressure

Distillation



http://www.chem1.com

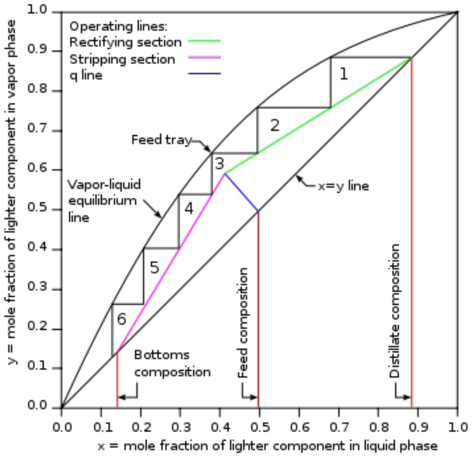
Distillation diagrams: plot of boiling temperatures as a function of liquid composition (at constant pressure, usually 1 atm) and of the corresponding vapor composition.

-Check that vapor is richer in the more volatile component

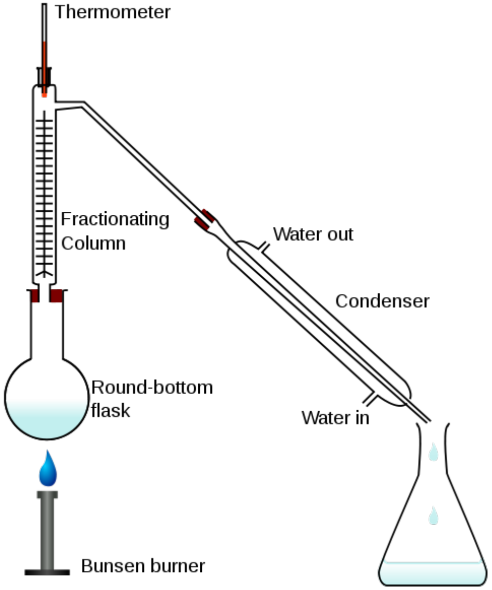
Fractional distillation:

-Successive evaporation and condensation operations in a single device (distillation column)

-Separates two liquids with similar boiling points



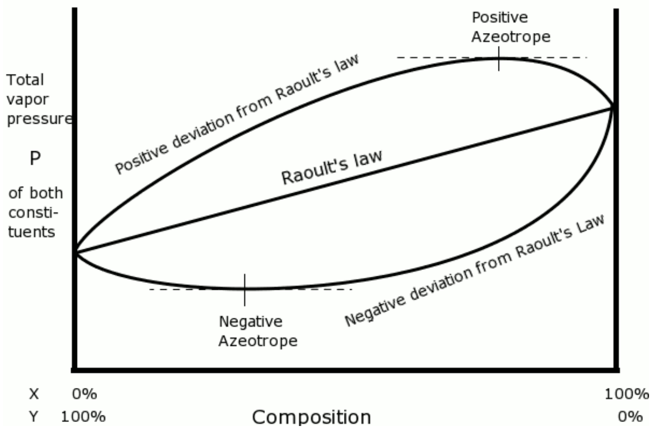
http://en.wikipedia.org/wiki/McCabe%E2%80%93Thiele_method



https://commons.wikimedia.org/wiki/File:Fractional_distillation_lab_apparatus.svg

Binary solutions: azeotropes

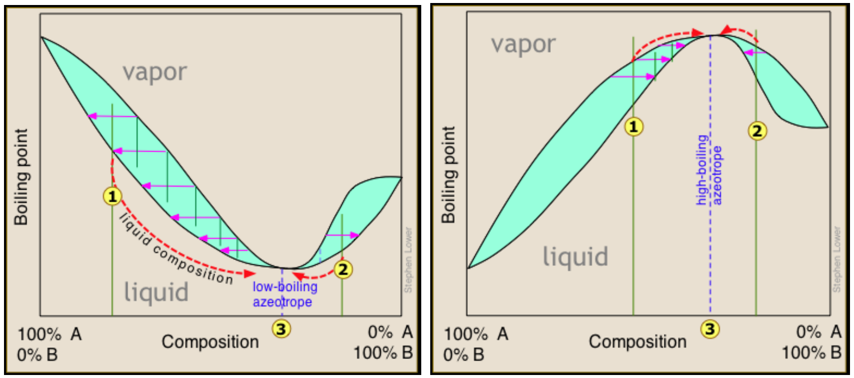
Most mixtures of liquids do not follow Raoult’s law.



http://en.wikipedia.org/wiki/File:RaoultDeviationPressureDiagram.png

Benzene-ethanol have a positive solution enthalpy (endothermic): Positive deviation

Acetone-chloroform have a negative solution enthalpy (exothermic): Negative deviation



http://www.chem1.com/acad/webtext/solut/solut-5.html

Benzene-ethanol. Since this system presents a maximum vapor pressure it will show a MINIMUM boiling temperature

Acetone-chloroform. Since this system presents a minimum vapor pressure it will show a MAXIMUM boiling temperature

T and x at which maximum or minimum T_b is found are called <u>azeotrope temperature and azeotrope composition</u>

A question to think about: is it possible to separate by fractional distillation azeotropic mixtures?